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3. That the attached is, to the best of RWS Group plc knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in Germany on 18 December 1998 under the number 198 58 662.0 and the official certificate attached hereto.

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For and on behalf of RWS Group plc

The 17th day of January 2003

19 FEDERAL REPUBLIC OF GERMANY

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The following details have been taken from the documents submitted by the Applicant

54 Feinteilige Suspensionen schwerlöslicher Calciumsalze und deren Verwendung in Zahnpflegemitteln

57 Suspensionen von wenig wasserlöslichen Calciumsalzen, ausgewählt aus Phosphaten, Fluoriden und Fluorphosphaten in flüssigen Medien, bevorzugt in Wasser mit suspendierten Primärteilchen mit Durchmessern von 5 bis 50 Nanometern und Längen von 10 bis 150 Nanometern, werden durch einen Gehalt von wenigstens 0,01 Gew.-%, bezogen auf das Gewicht der Suspension, eines wasserlöslichen Tensids oder eines wasserlöslichen polymeren Schutzkolloids gegen Agglomeration stabilisiert. Die Suspensionen eignen sich als remineralisierende Komponente in Zusammensetzungen zur Reinigung und Pflege der Zähne.

54 Fine suspensions of poorly soluble calcium salts and their use in dental care products

57 Suspensions of poorly water-soluble calcium salts, chosen from phosphates, fluorides and fluorophosphates, in liquid media, preferably in water, containing suspended primary particles having diameters of from 5 to 50 nanometers and lengths of from 10 to 150 nanometers are stabilized against agglomerization by a content of at least 0.01% by weight, based on the weight of the suspension, of a water-soluble surfactant or of a water-soluble polymeric protective colloid. The suspensions are suitable as remineralizing components in compositions for the cleaning and care of teeth.

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Description

The invention relates to fine suspensions of poorly soluble calcium salts which, because of their particle size in the nanometer range and their stability toward agglomeration, are particularly suitable for use in dental care products.

Phosphate salts of calcium have for a long time been added either as abrasive components or to promote remineralization of tooth enamel to formulations of dental cleaning products and dental care products. This is true particularly for hydroxylapatite and fluorapatite, and for amorphous calcium phosphates and for brushite (dicalcium phosphate dihydrate). However, calcium fluoride has also been described a number of times as a constituent of dental cleaning products and as a component for strengthening tooth enamel and for the prophylaxis of caries.

The availability of these substances for the desired remineralization depends quite decisively on the particle size of these poorly water-soluble components dispersed in the dental care products. It has therefore been proposed to use these poorly soluble calcium salts in extremely fine dispersion.

DE-A-2134862 discloses, for example, a dental care product for hypersensitive teeth which comprises very finely divided hydroxylapatite ($Ca_5[(PO_4)_3OH]$) whose particle size, however, is given as 6-8 µm (micrometers) since greater finenesses cannot be achieved by grinding.

Dental care products comprising separate components have also already been proposed, of which one comprises a dissolved Ca salt and the other comprises a dissolved phosphate or fluoride salt, and which are combined only shortly prior to application - or which are used in

succession - in order to apply the freshly precipitated and still amorphous or finely crystalline calcium salts to the tooth surface. The disadvantages of such handling are obvious since the user has to use two products successively or combine them shortly before use. If compositions which comprise freshly precipitated, still amorphous calcium phosphates or calcium fluoride are stored, the precipitates age, the crystallites grow and agglomerate to give coarser secondary particles. This reduces the remineralizing action and jeopardizes the stability of the dispersion.

The object was therefore to provide suspensions of such poorly soluble calcium salts whose particle size is in the nanometer range and which are largely protected against agglomeration.

WO 94/04460 A1 describes a process for the preparation of amorphous calcium salts and their use for the remineralization of teeth. EP 786245 A1 describes dental care products which comprise hydroxylapatite having particle sizes of from 0.05 to 1.0 µm which are obtained by grinding. WO 98/18719 discloses a hydroxylapatite composition which comprises hydroxylapatite with particle diameters of 10-20 nm and particle lengths of 50-100 nm and which are intended to be used, for example, in toothpastes. These are obtained by concentrating very dilute suspensions by two or more filtration steps.

EP 0499299 A2 discloses suspensions of particles of crystalline drugs which have a size of less than 100 nm and contain, adsorbed on their surface, a surface modifier which may also be a surfactant or a polymeric protective colloid. Stabilization of inorganic poorly soluble salts obtained by precipitation reactions is not disclosed. WO 96/34829 A1 discloses a process for the preparation of little-agglomerated particles in the nanometer range, in which a suspension of such

particles is prepared from the precursors in a liquid medium which has no noteworthy solvency for the particles, in the presence of a surface-blocking substance. In another embodiment, a sol which comprises amorphous or partially crystalline nanoparticles is suspended in the presence of the surface-blocking substance. Also named as surface-blocking substances are (poly)carboxylic acids and nonionogenic surfactants. Disclosed as suitable particles are, however, only oxide (hydrates), sulfides, selenides, tellurides and phosphides precipitated from hydrolyzable salts or organometallic compounds by adding water or changing the pH. Phosphates or fluorides of calcium or use of the suspensions in dental care products are not disclosed.

It has now been found that suspensions of poorly water-soluble calcium salts in very finely divided form can be stabilized during the precipitation or shortly thereafter if the precipitation is carried out in the presence of an agglomeration inhibitor, or the dispersion is redispersed in the presence of the agglomeration inhibitor.

The invention therefore provides a suspension of poorly water-soluble calcium salts, chosen from phosphates, fluorides and fluorophosphates, in a liquid medium in which these calcium salts are insoluble or poorly soluble, characterized in that the calcium salts are present in the form of primary particles having diameters of from 5 to 50 nanometers and lengths of from 10 to 150 nanometers and are stabilized against agglomerization by a content of at least 0.01% by weight, based on the weight of the suspension, of a water-soluble surfactant or of a water-soluble polymeric protective colloid.

Poorly soluble or poorly water-soluble salts are to be understood as meaning those salts which are soluble in

water or in the liquid suspension medium to an amount of less than 1 g/l (20°C). Suitable salts are preferably calcium hydroxyphosphate ($Ca_5[OH(PO_4)_3]$) or hydroxylapatite, calcium fluorophosphate, ($Ca_5[F(PO_4)_3]$) or fluorapatite, F-doped hydroxylapatite of the general composition $Ca_3(PO_4)_3(OH,F)$ and calcium fluoride (CaF_2) or fluorite (fluorspar).

A suitable liquid medium in which the calcium salts can be dispersed is primarily water. However, the calcium salt particles isolated from an aqueous suspension, e.g. by filtration or centrifugation, can also be redispersed in organic solvents and, in this case, likewise produce suspensions of the primary particles in the nanometer range which have virtually no tendency for agglomeration. Suitable organic liquid media are, for example, water-soluble, lower alcohols and glycols, polyethylene glycols, glycerol or mixtures thereof with one another or with water.

Primary particles are understood here as meaning the crystallites, i.e. the individual crystals, of said calcium salts. The particle diameter should be understood here as meaning the smallest diameter, and the length to be understood as meaning the greatest diameter of the crystal particles, e.g. the length of a rod-shaped crystallite. Wherever an average particle diameter is discussed, this is understood as meaning a volume-averaged value.

For the purposes of the present invention, water-soluble surfactants are understood as meaning all surface-active substances characterized by a lipophilic alkyl, alkylphenyl or acyl radical having 8-22 carbon atoms and a hydrophilic, ionic or nonionic group which imparts to the surfactant a solubility in water of more than 1 g/l (20°C). Suitable as anionic surfactants are, for example, the alkali metal or ammonium salts of C_8-C_{18}-alkanecarboxylic acids (soaps), of alkyl-(C_{12}-C_{18})

sulfuric monoesters (alkyl sulfates), of alkylpolyglycol ether sulfuric monoesters (ether sulfates), of sulfosuccinic mono-C_8-C_{18}-alkyl esters (sulfosuccinates), of alkanesulfonic acids (alkanesulfonates), of C_{12}-C_{18}-acyloxyethanesulfonic acids (isethionates), of C_{12}-C_{18}-acylaminoalkanesulfonic acids (taurides), of N-C_{12}-C_{18}-acylsarcosine (sarcosinates), of alkylpolyglycol ether carboxylic acids (ether carboxylates), of alkyl(polyglycol ether) phosphoric acids (alkyl(polyglycol ether) phosphate [sic]).

Suitable cationic surfactants are, for example, alkyltrimethylammonium chloride, alkyldimethylbenzyl-ammonium chloride, alkylpyridinium chloride, alkyldimethylhydroxyethylammonium chloride, acylimidazolinium methosulfates and acyloxyethyltrimethylammonium chloride.

Suitable zwitterionic surfactants are, for example, betaine surfactants, such as, for example, alkyldimethylcarboxymethylbetaine and acylaminoalkyldimethylcarboxymethylbetaine.

Amphoteric surfactants, such as, for example, alkylaminopropanecarboxylic acid [sic], are also suitable as ionic surfactants.

However, the nonionic surfactants are preferably suitable, in particular the addition products of ethylene oxide to lipids with mobile hydrogen atoms. Such suitable nonionic surfactants are, for example, the addition products of 6-60 mol of ethylene oxide to linear fatty alcohols, to fatty acids, to fatty amines, to fatty acid monoglycerides, to sorbitan fatty acid monoesters, to alkylphenols, to sugar fatty acid monoesters, to methylglucoside fatty acid monoesters and to fatty acid monoethanolamides. Further preferably suitable nonionic surfactants are the alkyl (oligo)

glucosides obtainable by reacting glucose with C_8-C_{18}-fatty alcohols or by transacetylation of butyl(oligo) glucoside with fatty alcohols. Preferably suitable alkyl (oligo) glucosides are, for example, the alkyl (C_8-C_{16}) glucosides having average degrees of oligomerization (of the glucoside radical) of from 1 to 2. Such products are [lacuna] commercially, e.g. under the trade name Plantacare® 1200 or Plantacare® 600. Further preferably suitable nonionogenic surfactants are the mixtures obtainable by ethoxylation of hydrogenated castor oil which are obtained, for example, by the addition of 30, 40 or 60 mol of ethylene oxide to hydrogenated castor oil.

Finally, amine oxide surfactants and sugar fatty acid esters are also suitable as nonionogenic surfactants.

Water-soluble polymeric protective colloids are understood as meaning high molecular weight compounds which are adsorbed on the surface of the nanoparticles and modify these such that they are hindered from coagulating and agglomerating. Suitable polymeric protective colloids are, for example, natural water-soluble polymers, such as, for example, gelatin, casein, albumin, starch, plant gums and water-soluble derivatives of water-insoluble polymeric natural substances, such as, for example, cellulose ethers (methylcellulose, hydroxyethylcellulose, carboxymethyl-cellulose), hydroxyethylstarch or hydroxypropylguar.

Synthetic water-soluble polymers suitable as protective colloids are, for example, polyvinyl alcohol, polyvinylpyrrolidone, polyacrylic acids, polyaspartic acid and others.

The suspensions according to the invention are prepared by precipitation reactions from aqueous solutions of water-soluble calcium salts and aqueous solutions of water-soluble phosphate or fluoride salts. Here the

precipitation is carried out in the presence of water-soluble surfactants or water-soluble polymeric protective colloids. This may, for example, be carried out by adding the surfactants or protective colloids to the aqueous phosphate or fluoride salt solution or to the solution of the calcium salt prior to the reaction. Alternatively, the aqueous calcium salt solution can be added to an aqueous surfactant or protective colloid solution at the same time as the phosphate or fluoride salt solution.

A further process variant involves the precipitation being carried out from a strongly acidic solution of a water-soluble calcium salt and a stoichiometric amount of a water-soluble phosphate salt with a pH below 3 by increasing the pH using an aqueous alkali or ammonia in the presence of water-soluble surfactants or water-soluble polymeric protective colloids.

The concentration of poorly soluble calcium salt in the suspensions according to the invention can cover a wide range from about 1 to 40% by weight. Here, the content can be increased on the one hand during the preparation by means of the concentration of the water-soluble salts, and on the other hand after the precipitation reaction by concentration, e.g. by filtration or centrifugation or by distilling off some of the water, without the effect of the surfactant or of the protective colloid being lost in the process.

The concentration of the surfactant or of the polymeric protective colloid in the aqueous suspension is, for example, 0.1 to 20% by weight, preferably 0.1-10% by weight, based on the content of poorly soluble calcium salt. In a preferred embodiment, the suspension according to the invention therefore comprises 1-40% by weight of the poorly soluble calcium salts and, for the stabilization, 0.1-10% by weight of a water-soluble

surfactant or of a water-soluble polymeric protective colloid, based on the weight of the calcium salt.

Preferably suitable for the stabilization against agglomeration are predominantly the nonionic surfactants in an amount of from 1 to 10% by weight, based on the weight of the calcium salt. The nonionic surfactants of the type of alkyl C_8-C_{16}-(oligo)-glucosides and of ethoxylates of hydrogenated castor oil have proven particularly effective. These can also be used together with the polymeric protective colloids for the stabilization.

For the preparation of suspensions according to the invention in other liquid media, it is expedient to start from aqueous suspensions according to the invention, free these by filtration or centrifugation from the aqueous phase, dry, where appropriate, the nanoparticles and redisperse them in organic solvents. Here, a fresh addition of surfactants or protective colloids is no longer necessary since the nanoparticles comprise the amounts of stabilizer required for inhibition of agglomeration adsorbed on the surface. The finely divided nature and stability of such suspensions is therefore comparable with those of the aqueous suspensions. Another possibility consists in mixing the aqueous suspension with a higher-boiling solvent, e.g. with glycerol, and removing the water by distillation. Suitable as organic liquid medium is, particularly with regard to use in dental care products, primarily glycerol and its liquid mixtures with sorbitol and optionally with water.

The suspensions according to the invention, in particular those of hydroxylapatite, fluorapatite and calcium fluoride, are suitable as remineralizing component for the preparation of compositions for the cleaning and care of teeth. As a result of the particularly finely divided nature, the effect, known

per se, of strengthening the tooth enamel and closing lesions and dentinal tubules can take place particularly rapidly and completely. The compositions for the cleaning and care of teeth may here be in the form of pastes, liquid creams, gels or mouthwashes. Even in liquid preparations, the suspensions according to the invention disperse readily and the calcium salts remain stably dispersed and do not tend toward sedimentation.

A preferred embodiment are, however, toothpastes with a content of silica, polishing agents, humectants, binders and aromas which comprise 0.1-5% by weight of finely divided calcium salts from the group hydroxylapatite, fluorapatite and calcium fluoride in the form of a suspension according to the invention.

The preparations for the cleaning and care of teeth can comprise the customary components and auxiliaries of such compositions in the amounts customary for this purpose. For toothpastes, these are, for example,

- cleaning and polishing substances, such as, for example, chalk, silicas, aluminum hydroxide, aluminum silicates, calcium pyrophosphate, dicalcium phosphate, insoluble sodium metaphosphate or synthetic-resin powder
- humectants, such as, for example, glycerol, 1,2-propylene glycol, sorbitol, xylitol and polyethylene glycols
- binders and consistency regulators, e.g. natural and synthetic water-soluble polymers and water-soluble derivatives of natural substances, e.g. cellulose ethers, phyllosilicates, finely divided silicas (aerogel silicas, pyrogenic silicas)
- aromas, e.g. peppermint oil, spearmint oil, eucalyptus oil, aniseed oil, fennel oil, caraway oil, menthyl acetate, cinnamaldehyde, anethole, vanillin,

thymol and mixtures of these and other natural and synthetic aromas

- sweeteners, such as, for example, saccharin-sodium, sodium cyclamate, aspartame, acesulfame K, stevioside, monellin, glycyrrhicine, dulcin, lactose, maltose or fructose
- preservatives and antimicrobial substances, such as, for example, p-hydroxybenzoates, sodium sorbate, triclosan, hexachlorophene, phenylsalicylates, thymol etc.
- pigments, such as, for example, titanium dioxide or pigment dyes for producing colored stripes
- buffer substances, e.g. primary, secondary or tertiary alkali metal phosphates, citric acid/Na citrate
- wound-healing and antiinflammatory active ingredients, e.g. allantoin, urea, azulene, panthenol, acetylsalicylic acid derivatives, plant extracts, vitamins, e.g. retinol or tocopherol.

The examples below serve to illustrate the subject-matter of the invention in more detail:

Exampl s

1. Preparation of suspensions of poorly soluble calcium salts

1.1 Preparation of a hydroxylapatite suspension by precipitation and redispersion

50.86 g of $Ca(NO_3)_2 \cdot 4H_2O$ were dissolved in demin. water and made up to 200 ml. 10 g of Plantacare 1200® were added to this. 60 ml of 25% strength ammonia solution were then added, so that the pH was 12.

17 g of ammonium hydrogenphosphate with dissolved in demin. water and made up to 200 ml. 10 g of Plantacare 1200® were added to this. 60 ml of 25% strength ammonia solution were then added.

Both solutions were brought to 75°C and mixed with vigorous stirring. After stirring for one hour, the precipitate was centrifuged off, washed a number of times with water and then taken up in water to give a 5% strength by weight hydroxylapatite suspension. The particle sizes were 4-10 nm × 60-130 nm (diameter × length).

(demin. = demineralized)

1.2 Preparation of a hydroxylapatite suspension by reprecipitation (pH shift) and concentration by evaporation

25.43 g of $Ca(NO_3)_2 \cdot 4H_2O$ were dissolved in demin. water and made up to 100 ml. 8.5 g of ammonium hydrogenphosphate were likewise dissolved in demin. water and made up to 100 ml. The solutions were combined, with formation of a voluminous precipitate. 37% strength hydrochloric acid was added dropwise to the suspension until the precipitate had completely dissolved at pH 2.

A mixture of 200 ml of demin. water, 200 ml of 25% strength ammonia solution and 20 g of Cremophor RH 60® (BASF, castor oil + 60 EO) was initially introduced. At 0°C, the apatite solution was added dropwise to this

solution with stirring, with formation of a precipitate. Excess ammonia was separated off by distillation, then the mixture was washed by means of dialysis until nitrate-free. Concentration by evaporation on a rotary evaporator gave a 10% strength by weight suspension of hydroxylapatite. The particle sizes were 30 nm (volume-averaged) in diameter (determination using a Micro-Trac 3.150 Ultrafine Particle Analyzer 150 by averaging over the total particle volume).

1.3 Preparation of a suspension of hydroxylapatite analogously to Example 1.2 (starting from $CaCl_2$)

11.95 g of calcium chloride were dissolved in demin. water and made up to 100 ml. 7.4 g of ammonium hydrogenphosphate were likewise dissolved in demin. water and made up to 100 ml. The solutions were combined with formation of a voluminous precipitate. 37% strength hydrochloric acid was added dropwise to the suspension until the precipitate had completely dissolved at pH 2.

A mixture of 200 ml of demin. water, 200 ml of 25% strength ammonia solution and 20 g of Cremophor RH 60® (BASF, castor oil + 60 EO) was initially introduced. At 0°C, the apatite solution was added dropwise to this solution with stirring, with formation of a precipitate. Excess ammonia was separated off by distillation, then the mixture was washed by means of dialysis until nitrate-free. Concentration by evaporation on a rotary evaporator gave a 10% strength by weight suspension of hydroxylapatite. The particle sizes were 10-35 nm × 20-50 nm (diameter × length).

1.4 Preparation of the hydroxylapatite suspension analogously to Example 1.2 using Arlatone 289 (BASF)

Instead of 20 g of Cremophor RH 60, 35 g of Arlatone 289 were used. A 10% strength by weight suspension of hydroxylapatite with an average particle size of 40 nm

was obtained. (Micro-Trac 3.150 Ultrafine Particle Analyzer).

1.5 Preparation of a hydroxylapatite suspension in glycerol

0.3 mol of calcium chloride were dissolved in 2000 ml of demin. water and thermostatted at 25°C. Ammonia solution was used to establish a pH of 12. Then, with vigorous stirring, a solution of 0.18 mol of ammonium hydrogenphosphate in 400 ml of demin. water, which was thermostatted at 25°C and had been adjusted to pH 10 using ammonia, was slowly added dropwise. After a reaction time of 20 h, 3 g of Cremophor RH 60® solution (40% strength by weight in demin. water) were added and dispersed by inputting chemical energy (stirring, ultrasound). The suspension was then centrifuged off a number of times and washed firstly with 1% strength aqueous Cremophor RH60® solution, then with ethanol. The material was then taken up in 100 ml of glycerol. Hydroxylapatite particles with sizes of 5-20 nm × 10-70 nm (diameter × length) were present in this glycerol suspension.

1.6 Preparation of a suspension of fluorine-doped hydroxylapatite in glycerol

0.3 mol of calcium chloride were dissolved in 2000 ml of demin. water and thermostatted at 25°C. Ammonia solution was used to establish a pH of 12. For this, a solution of 2.27 g of ammonium fluoride in 50 ml of demin. water was added. Then, with vigorous stirring, a solution of 0.18 mol of ammonium hydrogenphosphate in 400 ml of demin. water, which was thermostatted at 25°C and had been adjusted to pH 10 using ammonia, was slowly added dropwise. After a reaction time of 20 h, 3 g of Cremophor RH 60® solution (40% strength by weight in demin. water) were added and dispersed by inputting chemical energy (stirring, ultrasound). The suspension was then centrifuged off a number of times and washed firstly with 1% strength aqueous Cremophor

RH60® solution, then with ethanol. The material was then taken up in 100 ml of glycerol. Here, a glycerol suspension of $Ca_5(PO_4)_3(OH,F)$ particles with a size of 5-20 nm × 10-70 nm (diameter × length) was obtained.

1.7 Preparation of a calcium fluoride suspension by precipitation

11.95 g of anhydrous $CaCl_2$ were dissolved in demin. water made up to 100 ml. 200 ml of demin. water, 35 g of Arlatone 289 (BASF) and 15 g of ammonium fluoride were mixed in a receiver. Both solutions were cooled to 0°C and the first solution was added to the second with vigorous stirring. The dispersion formed was concentrated by evaporation on a rotary evaporator at 70°C until the solids content was 10% by weight. Washing was then carried out by means of dialysis. This gave a calcium fluoride suspension with an average (volume-weighted) particle size of 20 nm.

2. Dental creams with calcium salt nanoparticles

Formulation examples	**2.1**	**2.2**
Sident® 8	10.0% by wt.	10.0% by wt.
Sident® 22S	7.0% by wt.	7.0% by wt.
Sipernat® 320DS	0.8% by wt.	0.8% by wt.
CaF_2 suspension Example 1.7	5.0% by wt.	-
Hydroxylapatite suspension Example 1.1	-	5.0% by wt.
Polywax 1550	2.0% by wt.	2.0% by wt.
Texapon K 1296	1.5% by wt.	1.5% by wt.
Titanium dioxide	1.0% by wt.	1.0% by wt.
Cekol 500 T	1.0% by wt.	1.0% by wt.
Na fluoride	0.33% by wt.	0.33% by wt.
Na benzoate	0.25% by wt.	0.25% by wt.
Aroma	1.0% by wt.	1.0% by wt.
Tagat S	0.2% by wt.	-
Na saccharinate	0.15% by wt.	0.15% by wt.
Trisodium phosphate	0.10% by wt.	0.10% by wt.

Sorbitol (70% strength in water)	31.0% by wt.	31.0% by wt.
Water	ad 100% by wt.	ad 100% by wt.

The following commercial products were used:

Plantaren® 1200: C_{12}-C_{16}-fatty alcohol oligo-(1.4)-glucoside about 50% by weight in water
Manufacturer: HENKEL KGaA

Cremophor® RH 60: Castor oil (hydrogenated) poly(60)-glycol ether
Manufacturer: BASF

Arlatone® 289: Castor oil (hydrogenated) poly(54)-glycol ether
Manufacturer: Atlas Chemie (ICI)

Sident® 8: Synth. amorph. silica, BET 60 m^2/g
Tamped density: 350 g/l
Manufacturer: DEGUSSA

Sident® 22 S: Hydrogel silica, BET 140 m^2/g
Tamped density: 100 g/l
Manufacturer: DEGUSSA

Polywax® 1550: Polyethylene glycol, MW: 1550
Softening point 45-50°C
Manufacturer: RWE/DEA

Texapon® K 1296: Sodium lauryl sulfate powder
Manufacturer: HENKEL KGaA

Cekol® 500 T: Sodium carboxymethylcellulose
Viscosity (2% strength in water, Brookfield LVF 20°C): 350-700 mPas
Supplier: Nordmann-Rassmann

Tagat® S: Polyoxyethylene-(20) glyceryl monostearate
Manufacturer: Tego Cosmetics (Goldschmidt)

Patent claims

1. A suspension of poorly water-soluble calcium salts, chosen from phosphates, fluorides and fluorophosphates, in a liquid medium in which these salts are insoluble or poorly soluble, characterized in that the calcium salts are present in the form of primary particles having diameters of from 5 to 50 nanometers and lengths of from 10 to 150 nanometers and are stabilized against agglomerization by a content of at least 0.01% by weight, based on the weight of the suspension, of a water-soluble surfactant or of a water-soluble polymeric protective colloid.

2. The suspension as claimed in claim 1, characterized in that 1 to 40% by weight of the poorly soluble calcium salts and, for the stabilization, 0.1 to 10% by weight, based on the weight of the poorly soluble calcium salt, of a water-soluble surfactant or of a water-soluble polymeric protective colloid are present in the suspension.

3. The suspension as claimed in claim 1 or 2, characterized in that, for the stabilization, nonionic surfactants are present in an amount of from 1 to 10% by weight, based on the weight of the poorly soluble calcium salt.

4. A process for the preparation of the suspension as claimed in claim 1-3 by precipitation processes from aqueous solutions of water-soluble calcium salts and aqueous solutions of water-soluble phosphate or fluoride salts, characterized in that the precipitation is carried out in the presence of water-soluble surfactants or water-soluble polymeric protective colloids.

5. A process for the preparation of the suspension as claimed in claim 1-3 by precipitation from an acidic solution of a water-soluble calcium salt and a stoichiometric amount of a water-soluble phosphate salt with a pH below 3 by increasing the pH using aqueous alkalis or ammonia in the presence of water-soluble surfactants or water-soluble polymeric protective colloids.

6. The use of the suspension as claimed in any of claims 1-3 as remineralizing component in compositions for the cleaning and care of teeth.

7. A toothpaste with a content of silica polishing agents, humectants, binders and aromas, characterized in that 0.1-5% by weight of fine calcium salts from the group amorphous calcium phosphate, hydroxylapatite, fluorapatite and calcium fluoride are present in the form of a suspension as claimed in claim 1-3.